CHEMISTRY FACTIONS You Can't Afford to MISS!

Aldol condensation

Two molecules of aldehydes or ketones having α-hydrogen condense together in presence of base [dil. NaOH, Na2CO3, Ba(OH)₂] to form β-hydroxyaldehyde or β-hydroxyketone respectively which are collectively known as aldol.

2. Birch Reduction

In case of disubstituted alkynes reduction with sodium in liq. ammonia gives trans-alkene predominantly. This type of reduction is known as Birch-reduction.

$$CH_3 - C \equiv C - CH_3 \xrightarrow{\text{Na / liq. NH}_3} \xrightarrow{CH_3} C = C < \xrightarrow{H}_{\text{trans-But-2-ene}} CH_3$$

3. Beckmann Rearrangement

Oximes on treatment with catalyst such as conc. H2SO4, SOCl2, PCl5, etc. undergo rearrangement to form substituted amides. Reaction is known as 'Beckmann rearrangement'.

$$C_{6}H_{5} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{(i) \text{ Conc. } H_{2}\text{SO}_{4}} CH_{3} \xrightarrow{C} C-\text{NHC}_{6}H_{5}$$

$$\downarrow OH$$

$$syn-\text{Acetophenone}$$

4. Balz-Schiemann's reaction

This is the method to prepare fluorobenzene from benzene diazonium salt by first converting it to benzene diazonium tetrafluoroborate.

$$\begin{array}{c|c}
 & \uparrow \\
 & N \equiv NCI^{-} \\
 & \downarrow \\
 & HBF_{4} \\
 & -HCI
\end{array}$$

$$\begin{array}{c|c}
 & \uparrow \\
 & N \equiv NBF_{4}^{-} \\
 & \downarrow \\
 & \downarrow \\
 & + N_{2} + BF_{3}$$

Clemmensen Reduction

In this method, aldehydes and ketones are reduced with

Zn - Hg amalgam and conc. HCl.
$$\text{CH}_3\text{CHO} + 4\text{H} \xrightarrow{Zn - \text{Hg/HCl}} \text{CH}_3 - \text{CH}_3 + \text{H}_2\text{O}$$

$$\text{CH}_3\text{COCH}_3 + 4\text{H} \xrightarrow{Zn - \text{Hg/HCl}} \text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$$

Corey-House synthesis

In this reaction, an alkyl halide (1°, 2° or 3°) is first converted into lithium dialkyl copper and then reacted with another

alkyl halide (preferably 1°) to give corresponding alkane.

$$2R - X \xrightarrow{\text{Li}} 2R - \text{Li} \xrightarrow{\text{Cul}} R_2\text{CuLi} + \text{LiI}$$

Alkyl halide

 $R_2\text{CuLi} + R' - X \xrightarrow{\text{Plane}} R - R' + R\text{Cu} + \text{Li} X$

7. Cope elimination

Tertiary amines are not oxidised by KMnO₄. Their oxidation is carried out with Caro's acid or ozone or hydrogen

peroxide to form amine oxide.

$$R_3N \xrightarrow[3^{\circ} \text{Amine}]{\text{H}_2O_2 \text{ or } O_3} R_3NO^-$$

Amine-N-oxide

Tertiary amine oxide containing a β-hydrogen atom forms an alkene. This reaction is called Cope reaction or Cope

$$RCH_{2}CH_{2} - N \xrightarrow{\oplus} O^{\oplus} \xrightarrow{\Delta}$$

$$CH_{3} \qquad \downarrow$$

$$RCH = CH_{2} \qquad + \qquad CH_{3} > N - OH$$

Carbylamine Reaction

Primary amines both aliphatic and aromatic on heating with chloroform and alcoholic solution of potassium hydroxide form isocyanides or carbylamines which have an extremely unpleasant odour.

Ethylamine Chloroform

$$C_2H_5NH_2 + CHCl_3 + 3KOH (alc.) \xrightarrow{\Delta}$$
 $C_2H_5N \stackrel{\blacktriangle}{=} C + 3KCl + 3H_2O$

Ethyl isocyanide

9. Claisen—Schmidt reactions

It is a base catalyzed crossed aldol condensation in which an aromatic aldehyde condenses with aliphatic aldehyde or ketone. It is also known as simply *Claisen reaction*.

$$C_{6}H_{5}-C-H+CH_{3}-C-CH_{3} \xrightarrow{\text{dil. NaOH}} C_{6}H_{5}-CH-CH_{2}-C-CH_{3}$$
Benzaldehyde
$$C_{6}H_{5}-CH-CH_{2}-C-CH_{3}$$

$$C_{6}H_{5}-CH-CH-C-CH_{3}+H_{2}O \xrightarrow{C_{6}H_{5}-CHO} C_{6}H_{5}-CH-CH_{2}-C-CH_{3}$$
Dibenzal acetone

10. Cannizzaro Reaction

It is a self oxidation-reduction reaction in which aldehydes that do not have any α -hydrogen atom undergo disproportionation reaction (*i.e.* self-redox reaction) in the presence of 50% aqueous or ethanolic solution of alkali in which one of the molecule being reduced to alcohol and other being oxidised to the salt of corresponding acid.

11. Claisen condensation

Esters containing α -hydrogen atoms undergo self-condensation in presence of strong base like sodium ethoxide to give β -keto esters.

CH₃-C
$$\frac{O}{OC_2H_5}$$
+H $\frac{C}{OC_2H_5}$ $\frac{C_2H_5ONa}{O}$

Ethyl acetate

CH₃-C-CH₂COOC₂H₅+C₂H₅OH

Ethyl acetoacetate
(β-Ketoester)

12. Curtius rearrangement

In this method an acyl azide (obtained from reaction of carboxylic acid chloride and sodium azide), on heating in acidic or alkaline medium yields primary amine. The reaction involves an intermediate isocyanate which is hydrolysed to give primary amine.

hydrolysed to give primary amine.

$$R$$
—COOH $\xrightarrow{SOCl_2}$ $RCOCI$ $\xrightarrow{NaN_3}$ $RCON_3$ Acyl azide

 $RCON_3$ $\xrightarrow{-N_2}$ R —N=C=O $\xrightarrow{H_2O/H^+}$ R —NH₂ + CO₂

Isocyanate

13. Diels-Alder Reaction

This reaction involves the addition of a conjugated diene (4π -electron system) to an unsaturated compound called dienophile (2π -electron system) to yield a cyclic system.

$$\begin{array}{c} \text{CH}_{2} \\ \text{CH} \\ \text{CH}_{2} \\ \text{CH}_{3} \\ \text{CH}_{4} \\ \text{CH}_{2} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{4} \\ \text{CH}_{4} \\ \text{CH}_{5} \\ \text{C$$

14. Etard Reaction

Aromatic hydrocarbons on treatment with mild oxidising agents such as chromyl chloride CrO₂Cl₂ yield aldehydes.

15. Frankland Reaction

This is similar to Wurtz reaction with the difference that instead of sodium, zinc is used here in inert solvent.

$$R + X + Zn + X - R \longrightarrow R - R + ZnX_2$$

Dialkyl zinc compounds react with tertiary alkyl halides to give hydrocarbons with quaternary carbon atoms only.

$$(CH_3)_2Zn + (CH_3)_3CCl \longrightarrow (CH_3)_4C + CH_3ZnCl$$

16. Finkelstein reaction

Iodoalkanes can be conveniently prepared by treating alkyl chloride or bromides with sodium iodide in acetone or methanol. This is known as Finkelstein reaction.

17. Friedel-Crafts Reaction

Simple aromatic hydrocarbons can be converted to substituted hydrocarbons by reaction with alkyl halide in presence of Lewis acid like AlCl₃ or FeCl₃, etc.

18. Fries Rearrangement

Phenyl esters on heating with anhydrous AlCl₃ undergo Fries rearrangement in which acyl group (acetyl, benzoyl, etc.) migrates from phenolic oxygen to *ortho* or *para* position of benzene ring resulting in the formation of mixture of *o*- and *p*-hydroxyketone.

Gabriel phthalimide synthesis

Phthalimide on reaction with caustic potash forms potassium phthalimide which on treatment with alkyl halide gives *N*-alkyl phthalimide. This *N*-alkyl phthalimide on hydrolysis with hydrochloric acid yields primary amines.

20. Gattermann-Koch reaction

Benzene on reaction with a mixture of CO + HCl in presence of AlCl₃ forms benzaldehyde.

21. Hydroboration-Oxidation

Alkenes react with diborane to give alkyl boranes which on oxidation with hydrogen peroxide in presence of hydroxide forms alcohol.

$$R - CH = CH_2 \xrightarrow{B_2H_6} R - CH_2 - CH_2 - BH_2$$

$$RCH = CH_2$$

$$RCH_2CH_2$$

$$RCH_2$$

$$RC$$

22. Hunsdiecker reaction

This reaction involves the treatment of silver salt of carboxylic acid with bromine in refluxing CCl₄ to yield alkyl bromide with one carbon atom less than the original acid used.

with one carbon atom less than the original acid used.

$$CH_3CH_2COOAg + Br_2 \xrightarrow{CCl_4} CH_3CH_2Br + CO_2 + AgBr$$

23. Hofmann Mustard oil Reaction

This reaction is given by aliphatic and aromatic primary amines only, hence it can be used as a test for primary amines.

Ethylamine (1°) Carbon disulphide

$$C_2H_5N=C=S+HgS+2HC1 \stackrel{HgCl_2}{\longleftarrow} C_2H_5NH-C-SH$$

Ethyl isothiocyanate

Dithioethylcarbamic acid

Alkyl isothiocyanates have a characteristic unpleasant smell of mustard oil. Hence, this reaction is known as *Hofmann mustard oil reaction*.

24. Haloform reaction

Methyl ketones on oxidation with sodium hypohalite (NaOX *i.e.* NaOH + X_2) yield haloform along with sodium salt of carboxylic acid with one carbon atom less than the starting ketone.

$$R - C - CH_3 + 3I_2 + 4NaOH \xrightarrow{\Delta}$$

$$O$$

$$NaCl + RCOOH \xrightarrow{HCl} R - CONa + CHI_3 + 3NaI + 3H_2O$$

25. Hell-Volhard-Zelinsky reaction

(HVZ reaction - Halogenation)

Aliphatic carboxylic acids on reaction with bromine or chlorine in presence of small amount of red phosphorous produce α -haloacids.

$$\begin{array}{c} \text{Cl} \\ \text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{Cl}_2 + \text{Red P}} \\ \text{Propanoic acid} \end{array} \xrightarrow{\text{CH}_3} \begin{array}{c} \text{Cl} \\ \text{CH}_3 - \text{CH} - \text{COOH} - \text{COOH} \\ \text{acid} \end{array}$$

$$\begin{array}{c} \text{Cl} \\ \text{CH}_3 - \text{C} - \text{COOH} \xleftarrow{\text{Cl}_2 + \text{Red P}} \\ \text{Cl} \end{array}$$

26. Hofmann-bromamide reaction

Primary amides on reaction with bromine in presence of an alkali yield primary amine with one carbon atom less than the parent amide.

$$R$$
—CONH₂ + Br₂ + 4KOH $\xrightarrow{\Delta}$
 1° Amide R —NH₂ + 2KBr + K₂CO₃ + H₂O

27. Knoevenagel reaction

In this reaction, aldehydes and ketones condense with compounds containing active methylene group like acid (e.g. malonic acid), ester (e.g. acetoacetic ester, malonic ester) or nitrile, etc. leading to the formation of α , β -unsaturated compound.

CH₃ C=O + H₂C COOH (i) Pyridine/
$$\Delta$$

COOH (ii) H₃O⁺ H₃C - CH = CH - COOH + CO₂ + H₂O

28. Kolbe's Electrolytic Method

In this method, a concentrated solution of sodium or potassium salt of a carboxylic acid is electrolysed to give higher alkanes.

$$RCOOK + RCOOK \xrightarrow{Electrolysis} R - R + 2CO_2 + H_2 + 2KOH$$

29. Leuckart reaction

An aldehyde or ketone on heating with ammonium formate or ammonium formamide, undergoes reductive amination to form formyl derivative of primary amine which on hydrolysis either with acid or base yields primary amine.

$$R$$
 $C=O + 2HCOONH_4$
or
 $2HCONH_2$
 R
 $CHNHCHO + CO_2 + NH_3 + H_2O$

30 Meerwein-Ponndorf-Verley reduction

In this reaction, ketones are reduced to secondary alcohols on heating with *iso*-propyl alcohol in presence of catalyst aluminium isopropoxide. In the reaction *iso*-propyl alcohol gets oxidised to acetone.

ets oxidised to acetone.

$$R > C = O + CH_3 > CH - OH \frac{[(CH_3)_2CHO]_3A]}{CH_3}$$

Ketone

 $R > CH - OH + CH_3 > C = O$
 $R > CH - OH + CH_3 > C = O$
 $R > CH - OH + CH_3 > C = O$

Acetone

31. Ozonolysis

Ozone on passing through a solution of alkenes in an inert solvent like CCl_4 or $CHCl_3$ at low temperature oxidises the alkene to a cyclic product called ozonide which is unstable and on reduction with reducing agents like zinc and water or hydrogen in presence of palladium gives aldehydes and/or ketone depending upon structure of alkene, i.e., >C = part of the alkene gets converted to >C = O.

$$>$$
C=C $<+O_3$ $\longrightarrow>$ C $<$ C $<$ Zn/H₂O $<$ 2 $>$ C=C

32. Oppenauer's oxidation

In this reaction, secondary alcohols are oxidised to ketones in a good yield using aluminium *tert*- butoxide in excess of acetone.

$$\begin{array}{c|c}
R > \text{CH-OH+CH}_3 - \text{C-CH}_3 \\
R' > 2^{\circ} \text{ alcohol}
\end{array}$$

$$\begin{array}{c|c}
C = \text{OH}_3 - \text{CH-CH}_3 \\
OH & \text{OH}_3 - \text{CH-CH}_3 \\
R' > C = \text{OHCH}_3 - \text{CH-CH}_3 \\
\text{Ketone}$$

$$\begin{array}{c|c}
I = \text{CH-CH}_3 - \text{CH-CH}_3 \\
I = \text{CH-CH}_3 - \text{CH-CH}_3 - \text{CH-CH}_3 \\
I = \text{CH-CH}_3 - \text{CH-CH}_3 - \text{CH-CH}_3 - \text{CH-CH}_3 \\
I = \text{CH-CH}_3 - \text{CH-CH}_$$

33. Oxo process

In this process, an alkene on heating with water gas (CO + H₂) under pressure in the presence of catalyst cobalt carbonyl hydride [CoH(CO)₄] yields aldehyde.

$$C = C + CO + H_2 \xrightarrow{[CoH(CO)_4]} - C - C - CHO$$

34. Perkin condensation

It is a condensation reaction in which an aromatic aldehyde condenses with aliphatic acid anhydride in presence of sodium salt of same acid to give a condensate which upon hydrolysis yields α,β -unsaturated acid.

$$C_{6}H_{5}-CH=\underbrace{O}_{H_{2}}CH-\underbrace{C}_{C}$$

$$CH_{3}-CD$$

$$CH_{3}-CD$$

$$CH_{3}-CD$$

$$CH_{3}-CD$$

$$CH_{2}O$$

$$CH_{3}-CD$$

$$CH$$

35. Reimer-Tiemann reaction

Concentrated solution of CHCl₃ reacts with phenol in presence of alc. KOH to yield salicylaldehyde.

36. Reformatsky reaction

It involves the reaction of zinc and α -halogenated ester, which add to carbonyl compound to yield β -hydroxy ester.

$$CH_{3}-C-CH_{3}+BrCH_{2}COOC_{2}H_{5} \xrightarrow{Zn}$$

$$OH \qquad OZnBr$$

$$CH_{3}-C-CH_{2}COOC_{2}H_{5} \xrightarrow{H_{2}O/H^{+}}CH_{3}-C-CH_{2}COOC_{2}H_{5}$$

$$CH_{3} \qquad CH_{3}$$

Ethyl-3-hydroxy-3-methyl butanoate

37. Rosenmund's reduction

Acid chlorides are reduced to aldehydes by palladised barium sulphate partially poisoned with sulphur or quinoline. (—COCl is reduced to —CHO)

$$R$$
— C — $Cl + H2 $\xrightarrow{Pd/BaSO_4} R$ — C — $H + HCl$$

38. Sandmeyer's reaction

In this reaction Diazonium salttract with CuX/HX and respective halide is formed.

$$\begin{array}{c}
\stackrel{+}{\text{N}} \equiv \text{NCI} & \xrightarrow{\text{CuCl/HCl}} & \xrightarrow{\text{Cl}} \\
\downarrow & & \downarrow \\
& \downarrow \\
& & \downarrow \\
& & \downarrow \\
&$$

39. Schotten-Baumann reaction

Benzoylation of alcohols or phenols in presence of NaOH is called Schotten-Baumann reaction.

40. Stephen's reduction

In this reaction cyanides are reduced to aldehyde in pressure of SnCl2/H4 followed by hydrolysis.

$$R-C \equiv N \xrightarrow{\text{SnCl}_2 + \text{HCl}} R \xrightarrow{\text{Ether}} R \xrightarrow{\text{C}} \text{NH}_2\text{Cl} \xrightarrow{\text{H}_2\text{O}}$$

$$R \xrightarrow{\text{Aldimine}} \text{NH}_2\text{Cl} \xrightarrow{\text{H}_2\text{O}}$$

$$R \xrightarrow{\text{RCHO}} + \text{NH}_4\text{Cl} \xrightarrow{\text{Aldehyde}}$$

41. Schmidt's reaction

Carboxylic acids on heating with hydrazoic acid (HN3) at 50-55°C in presence of conc. H₂SO₄ produce primary amines with one carbon atom less than original carboxylic acid.

RCOOH + HN₃
$$\xrightarrow{\text{H}_2\text{SO}_4 \text{ (Conc.)}}$$
 RNH₂ + N₂ + CO₂

Carboxylic Hydrazoic

acid acid 1° Amine

42. Sabatier - Senderen's reaction

The method involves the reduction of unsaturated hydrocarbons (alkenes and alkynes) with nickel catalyst. Raney nickel is more reactive than supported nickel catalyst. $RCH = CH_2 + H_2 \xrightarrow{Ni} RCH_2CH_3$

$$RCH = CH_2 + H_2 \xrightarrow{N_1} RCH_2CH_3$$
Alkene
Alkane

43. Tischenko reaction

All aldehydes (with or without α-hydrogen atom) in presence of aluminium ethoxide, [Al(OC2H5)3] undergo simultaneous oxidation (to carboxylic acid) and reduction (to alcohol) to form an ester.

alcohol) to form an ester.

$$2RCHO \xrightarrow{Al(OC_2H_5)_3} = \begin{bmatrix} RCH_2OH + RCOOH \\ Alcohol & Carboxylic acid \end{bmatrix}$$
 $RCOOCH_2R \leftarrow$

44. Ullmann Reaction

Aryl halides especially iodides on reaction with copper metal yield biphenyls.

$$\begin{array}{c}
\text{Sealed} \\
\text{tube}
\end{array}$$

$$\begin{array}{c}
\text{Sealed} \\
\text{tube}
\end{array}$$

$$\begin{array}{c}
\text{Biphenyl}
\end{array}$$

45. Williamson's synthesis

Metal alkoxides on treatment with alkyl halides yield ethers. The reaction is known as Williamson's synthesis.

$$RO^{-} + Na^{+} + X + R' \xrightarrow{\Delta} R - O - R' + NaX$$
Ether

46. Wacker process

Alkenes are directly oxidised by the catalyst palladium chloride-cupric chloride (PdCl2-CuCl2) in the presence

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{PdCl_2-CuCl_2} CH_3 - CHO$$
Ethene
Ethene

47. Wolff-Kishner Reduction

In this method, aldehydes and ketones are reduced with hydrazine (NH2-NH2) and KOH.

$$R - C - CH_3 \xrightarrow{NH_2 - NH_2} R - C = NNH_2$$

$$\downarrow KOH/glycol$$

$$\downarrow or C_2H_5ONa$$

$$R - CH_2 - CH_3 + N_2$$

48. Wurtz Reaction

In this reaction, ether solution of alkyl halide is treated with sodium to form alkane.

$$R - X + 2Na + X - R$$
 Dry ether $R - R + 2NaX$

49. Wittig Reaction

It is an important reaction to change a carbonyl compound into alkene by treating carbonyl compound with a ylide. Ylides are the species which in their ground state have negative carbon adjacent to a positive heteroatom like P, As, Sb, etc. For example, phosphorus ylide, $Ph_3\overset{+}{P} - \overline{C}HR$. $R'CH = O + Ph_3\overset{+}{P} - \overline{C}HR \xrightarrow{THF or} R'CH = CHR + Ph_3PO$

Wohler's reaction

Acetylene is prepared by action of water on calcium carbide. This method is used for laboratory as well as industrial preparation.

$$CaC_2 + 2H_2O \longrightarrow CH \equiv CH + Ca(OH)_2$$

51. Wurtz-Fittig Reaction

When a mixture of aryl halide and alkyl halide reacts with sodium metal in dry ether, substituted arenes are obtained.

$$Cl + 2Na + Cl - CH_3 \xrightarrow{\text{other}} CH_3 + 2NaCl$$